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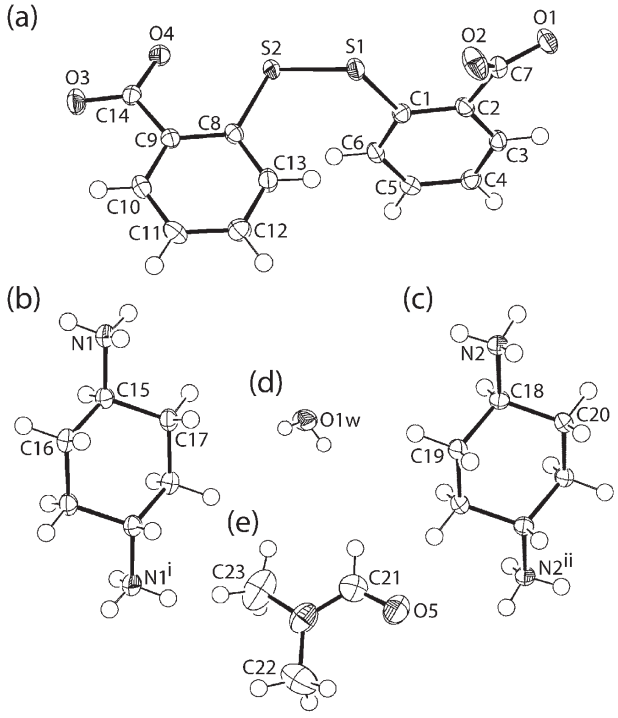
Crystal structure of cyclohexane-1,4-diammonium 2-[(2-carboxylatophenyl)disulfanyl]benzoate — dimethylformamide — monohydrate (1/1/1), $[C_6H_{16}N_2][C_{14}H_8O_4S_2]\cdot C_3H_7NO\cdot H_2O$



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Abstract

$[C_6H_{16}N_2][C_{14}H_8O_4S_2]\cdot C_3H_7NO\cdot H_2O$, triclinic, $P\bar{1}$ (no. 2), $a = 7.86120(10)$ Å, $b = 12.2464(2)$ Å, $c = 14.1615(2)$ Å, $\alpha = 111.293(1)°$, $\beta = 105.767(2)°$, $\gamma = 93.690(1)°$, $V = 1202.11(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0373$, $wR_{ref}(F^2) = 0.1054$, $T = 100(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.10 × 0.07 × 0.02 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	2.39 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	76.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	30359, 5016, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4635
$N(param)_{refined}$:	333
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title co-crystal salt was prepared through the solvent drop-assisted grinding of 2-mercaptobenzoic acid (2-MBA; Merck) and *N*,*N*-bis((pyridine-4-yl)methylene)-cyclohexane-1,4-diamine (4-PMCD) in a 1:1 molar ratio (0.001 mol, 0.154 g for 2-MBA and 0.001 mol, 0.292 g 4-PMCD). The former was used as received without purification, while the latter was prepared according to the literature procedure [5], M. pt. (Hanon MP-450); 480.7−481.4 K; lit. [5]: 481−482 K. The mixture was ground for 15 min in the presence of a few drops of methanol that lead to a yellow slurry. This was dissolved in dimethylformamide (2 mL) and carefully layered with the same volume of benzene. Yellow crystals were obtained approximately 1 week after the experiment. M. pt.: 441.5−443.9 K. **IR** (Bruker Vertex 70v; cm^{-1}): 3357−3275(w) ν(NH), 3048−2866(w) ν(CH), 1692(*m*) ν(C=O), 1584−1447(*s*) ν(C=C), 1367(*s*) ν(C−N), 735(*s*) ν(C=C).

Experimental details

The C-bound H atoms were geometrically placed (C−H = 0.95−1.00 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. The O- and N-bound H-atoms were located in difference Fourier maps but were refined with distance restraints of O−H = 0.84+−0.01 Å and N−H = 0.88+−0.01 Å, respectively, and with $U_{iso}(H)$ set to

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.47247(5)	−0.09550(3)	0.75674(3)	0.01450(11)
S2	0.46421(5)	0.06994(3)	0.75039(3)	0.01334(11)
O1	0.73605(16)	−0.39304(11)	0.72755(10)	0.0184(3)
O2	0.50258(19)	−0.31583(12)	0.76985(11)	0.0249(3)
O3	0.19676(17)	0.37981(11)	0.76832(10)	0.0200(3)
O4	0.44096(15)	0.29557(10)	0.78509(9)	0.0160(2)
C1	0.5042(2)	−0.18708(14)	0.63395(13)	0.0126(3)
C2	0.5723(2)	−0.29253(14)	0.62601(13)	0.0130(3)
C3	0.5971(2)	−0.36196(14)	0.52982(13)	0.0137(3)
H3	0.646027	−0.432120	0.524340	0.016*
C4	0.5526(2)	−0.33193(14)	0.44177(13)	0.0146(3)
H4	0.568503	−0.381703	0.376614	0.018*
C5	0.4844(2)	−0.22786(15)	0.45021(13)	0.0144(3)
H5	0.453322	−0.206110	0.390617	0.017*
C6	0.4618(2)	−0.15587(14)	0.54600(13)	0.0133(3)
H6	0.416767	−0.084383	0.551651	0.016*
C7	0.6073(2)	−0.33633(14)	0.71590(13)	0.0151(3)
C8	0.2286(2)	0.06397(14)	0.69131(13)	0.0122(3)
C9	0.1568(2)	0.16901(14)	0.70518(12)	0.0122(3)
C10	−0.0295(2)	0.15931(15)	0.66802(13)	0.0150(3)
H10	−0.079408	0.229846	0.679465	0.018*
C11	−0.1436(2)	0.04968(16)	0.61496(14)	0.0168(3)
H11	−0.270184	0.045257	0.592797	0.020*
C12	−0.0713(2)	−0.05358(15)	0.59448(14)	0.0170(3)
H12	−0.147843	−0.129176	0.554436	0.020*
C13	0.1133(2)	−0.04625(14)	0.63262(14)	0.0157(3)
H13	0.161982	−0.117333	0.618601	0.019*
C14	0.2723(2)	0.29144(14)	0.75705(12)	0.0128(3)
N1	0.0944(2)	0.56987(13)	0.72609(12)	0.0195(3)
H1N	−0.0130(18)	0.584(2)	0.7277(18)	0.023*
H2N	0.128(3)	0.5145(16)	0.7493(18)	0.023*
H3N	0.178(2)	0.6346(14)	0.7635(16)	0.023*
C15	0.0930(2)	0.52648(14)	0.61238(13)	0.0141(3)
H15	0.212534	0.504818	0.609576	0.017*
C16	−0.0516(2)	0.41505(14)	0.54447(13)	0.0150(3)
H16A	−0.168926	0.432639	0.553102	0.018*
H16B	−0.021943	0.350674	0.569311	0.018*
C17	0.0654(2)	0.62665(14)	0.57342(13)	0.0145(3)
H17A	0.167321	0.694092	0.616591	0.017*
H17B	−0.045980	0.655262	0.583449	0.017*
N2	0.65562(18)	0.52327(12)	0.88085(11)	0.0141(3)
H4N	0.578(2)	0.4563(12)	0.8439(15)	0.017*
H5N	0.597(3)	0.5768(15)	0.9131(16)	0.017*
H6N	0.691(3)	0.5457(18)	0.8353(14)	0.017*
C18	0.8100(2)	0.50552(14)	0.95961(13)	0.0129(3)
H18	0.764259	0.486933	1.012422	0.015*
C19	0.8883(2)	0.40004(14)	0.90183(13)	0.0144(3)
H19A	0.927510	0.414866	0.846082	0.017*
H19B	0.794557	0.327198	0.866282	0.017*
C20	0.9514(2)	0.61912(14)	1.01969(13)	0.0144(3)
H20A	0.898118	0.684828	1.059189	0.017*
H20B	0.992685	0.641863	0.968148	0.017*
O5	0.2162(2)	0.78571(13)	0.91767(12)	0.0323(3)
N3	0.1420(2)	0.96296(15)	0.91935(14)	0.0275(4)
C21	0.2513(3)	0.89438(19)	0.95340(17)	0.0290(4)
H21	0.362129	0.933309	1.008523	0.035*
C22	−0.0258(3)	0.9061(2)	0.83582(19)	0.0397(5)
H22A	−0.012743	0.900479	0.767406	0.060*
H22B	−0.118710	0.953060	0.850992	0.060*
H22C	−0.060425	0.825929	0.832038	0.060*
C23	0.2029(4)	1.0896(2)	0.9614(2)	0.0422(6)
H23A	0.314406	1.112284	1.021475	0.063*
H23B	0.110759	1.130991	0.986101	0.063*
H23C	0.225122	1.111792	0.905374	0.063*
O1W	0.48304(19)	0.68124(12)	0.00114(11)	0.0255(3)
H1W	0.404(3)	0.716(2)	−0.022(2)	0.038*
H2W	0.490(4)	0.699(2)	0.0654(10)	0.038*

1.5U_{eq}(O) and 1.2U_{eq}(N). The maximum and minimum residual electron density peaks of 1.16 and 0.45 eÅ^{-3}, respectively, were located 1.07 and 0.62 Å from the H22b and C23 atoms, respectively.

Comment

Recent co-crystallization studies involving isomeric Schiff bases appended with pyridyl donors, *i.e.* *N*,*N*′-bis((pyridine-n-yl)methylene)cyclohexane-1,4-diamines, for n = 2, 3 and 4, as coformers have resulted in the isolation of crystals whereby the original n = 2 species has been converted into a cyclohexane-1,4-diammonium di-cation, as in its salt with pyridine-2-carboxylate [6]. In another experiment, the n = 2 species was converted to a 2-(4-ammoniocyclohexyl)-3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-2-ylium dication in a salt with 2-[(2-carboxylatophenyl)disulfanyl]benzoate [7]. These experiments are doubly complicated as the isomeric *n*-mercaptobenzoic acids employed are also known to be susceptible to side reactions in co-crystallization experiments [8, 9]. In another example of an unexpected outcome of a co-crystallization experiment with these molecules, the title salt solvate hydrate was isolated from the 1:1 co-crystallization of (4-py)—CH=NC_6H_{10}N=CH—(4-py) and 2-mercaptobenzoic acid.

X-ray crystallography shows the product to comprise two independent cyclohexane-1,4-diammonium dications, each located about a centre of inversion, a 2-[(2-carboxylatophenyl) disulfanyl]benzoate di-anion, and a molecule each of dimethylformamide (DMF) and water (figure, 70% probability displacement ellipsoids with unlabelled atoms related by the symmetry operations i: $-x, 1-y, 1-z$ and ii: $2-x, 1-y, 2-z$). The cation/anion assignments are readily confirmed based on the pattern of hydrogen bonding in the crystal (see below) and in the near equivalence of the C7—O1, O2 [1.271(2), 1.247(2) Å] and C14—O3, O4 [1.248(2), 1.269(2) Å] bond lengths. Each

dication adopts a crystallographically imposed chair conformation so that the 1,4-ammonium groups are anti, typical for this cation [10]. The dianion is twisted as seen in the C1—S1—S2—C2 torsion angle of 91.42(8)°, and in the dihedral angle of 79.32(8)° formed between the two phenyl rings. The O1-carboxylate group is twisted significantly out of the plane of the phenyl ring to which it is bound as seen in C1—C2—C7—O1 torsion angle of −148.22(16)° and dihedral angle of 35.77(9)° between these residues. A significantly more co-planar relationship is evident for the O3-carboxylate with the C8—C9—C14—O3 torsion angle being −178.31(15)° and the dihedral angle being 4.84(13)°.

Significant hydrogen bonding occurs in the crystal, most being charge-assisted, which results in the stabilization of a three-dimensional architecture. The N1-dication forms donor interactions to carboxylate-O1 and O3 atoms as well as to the DMF-O5 atom [N1—H1n···O1^{iii}: H1n···O1^{iii} = 2.010(16) Å, N1···O1^{iii} = 2.887(2) Å with angle at H1n = 177(3)°; N1—H2n···O3: H2n···O3 = 1.86(2) Å, N1···O3 = 2.723(2) Å and angle = 168(2)°; N1—H3n···O5: H3n···O5 = 2.22(2) Å, N1n···O5 = 2.884(2) Å and angle = 132.0(15)° for symmetry operation iii: $-1+x$, $1+y$, z]. A similar pattern occurs for the N2-dication but, the third hydrogen bond is oriented to the water molecule [N2—H4n···O4: H4n···O4 = 1.944(17) Å, N2···O4 = 2.805(2) Å with angle at H4n = 166.9(16)°; N2—H5n···O1w^{iv}: H5n···O1w^{iv} = 1.90(2) Å, N2···O1w^{iv} = 2.772(2) Å with angle = 170.0(19)°; N2—H6n···O1^{v}: H6n···O1^{v} = 2.03(2) Å, N2···O1^{v} = 2.906(2) Å with angle = 171(2)°; for symmetry operations iv: x, y, $1+z$ and v: x, $1+y$, z]. The water molecule forms donor interactions to carboxylate-O4 and DMF-O5 atoms [O1w—H1w···O5^{vi}: H1w···O5^{vi} = 1.91(3) Å, O1w···O5^{vi} = 2.744(2) Å with angle at H1w = 176(3)°; O1w—H2w···O4^{vii}: H2w···O4^{vii} = 2.013(15) Å, O1w···O4^{vii} = 2.8237(18) Å with angle = 162(3)° for symmetry operations vi: x, y, $-1+z$ and vii: $1-x$, $1-y$, $1-z$]. In this scheme, there is no role for the carboxylate-O2 atom. However, it is noted that this atom accepts two weak hydrogen bonds from ammonium-N1 and N3 groups [N1—H3n···O2^{v}: H3n···O2^{v} = 2.554(17) Å, N1···O2^{v} = 3.217(2) Å with angle at H3n = 132.5(15)°; N2—H6n···O2^{v}: H6n···O2^{v} = 2.58(2) Å, N2···O2^{v} = 3.054(2) Å with angle = 114.5(18)°].

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